

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO CROSSLINKED POLYMERS

(71) We, GAF CORPORATION, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, of 140 West 51st Street, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to insoluble cross-linked copolymers formed on an inert substrate by the addition polymerization of monomers containing ethylenic unsaturation.

Polymers of N-vinyl lactams and particularly N-vinyl pyrrolidone have been heretofore produced in insoluble form. As used herein the term "insoluble" is intended to define products which are insoluble in water, strong mineral acids, caustic alkaline solutions and a range of organic solvents including hydrocarbons, chlorinated hydrocarbons, ethers ketones and esters. Illustrative insoluble polymers of N-vinyl lactams are those represented by the polyvinyl pyrrolidones of U.S. Patent Specifications 3,216,579; 2,927,913 and 3,511,823, as distinguished from the polyvinyl pyrrolidones such as represented by U.S. Patent Specifications 2,265,450 and 2,335,454.

Beverages such as beer are known to be subject to purification when contacted with inorganic clay carriers coated with a vinyl resin such as polyvinyl acetate or a poly N-vinyl pyrrolidone, as disclosed for example in U.S. Patent Specification 3,424,588, or with polyvinyl pyrrolidone which has been cross-linked or complexed with polyacids such as polyacrylic and tannic acids and their derivatives.

It has been found that polymeric selective adsorbents heretofore employed were not as effective as might be desired. A primary difficulty with these adsorbents is that they do not efficiently utilize the potentially available active sites. When employed as fine powders of the polymeric material, a large proportion of the potentially active sites is buried within the polymeric particle and is thus not available for adsorption. And, even when these polymers are coated on inert carriers by conventional coating techniques, the coating thickness is so great that a large proportion of the potentially active sites remain unavailable for adsorption.

According to the invention there is provided a method of forming an insoluble, cross-linked, polymeric coating having a degree of shape stability on an inert carrier comprising blending *in situ* as least one monomer capable of addition polymerization through an unsaturated bond, a comonomer which contains more than one polymerizable unsaturated bond and an inert carrier and copolymerizing the monomers forming an insoluble as hereinbefore defined cross-linked coating on the inert carrier, wherein the inert carrier is selected from zeolites, alkaline earth metal oxides, alkaline earth metal hydroxides, silicon rubber, silica gels, glasses, ion-exchange resins, diatomaceous earth and mixtures of two or more thereof, and the monomer or monomers capable of addition polymerization through an unsaturated bond is/are selected from substituted and unsubstituted amides of unsaturated carboxylic acids, substituted and unsubstituted esters of unsaturated carboxylic acids, vinyl ethers, N-vinyl lactams, vinyl esters, vinyl monomers containing basic nitrogen groups therein and co-polymerizable mixtures of two or more thereof.

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wherein R is hydrogen or an alkyl group containing from 1 to 20 carbon atoms; R_1 is the residuum of a mono-functional monomer capable of addition polymerization through an unsaturated bond; R_2 is the residuum of a difunctional monomer; m represents the number of moles or R_1 ; n represents the number of moles of the residuum of a N-vinyl lactam; and p represents the number of moles of R_2 ; where the ratio of m to n is within a range of from 0 to 1:1; and the ratio of $(m+n)$ to p is within a range of from 99.9:0.1 to 1:1.

Typical of the polyfunctional comonomers which can be employed in the polymers defined by the above formula are divinyl monomers including: divinyl benzene; methylene-bis-acrylamide; ethylidene-bis-vinyl pyrrolidone; divinyl ethers of polyalkylene glycol; divinyl ketone; conjugated diolefins such as butadiene, isoprene and mixtures thereof; diallyl compounds such as diallyl, diallyl ether, diallylphthalate and mixtures thereof; allylacrylates, such as allyl acrylate; triallylcyanurate; diacrylates of a polyalkylene glycol; etc.

The resin is present in combination with the carrier in an amount sufficient to achieve the desired result of hydration resistance and insolubility in the fluid containing the solute to be adsorbed. The ratio of polymer and carrier can range from 99:1 to 1:99, preferably from 90:10 to 10:90, depending upon the porosity of the carrier and the particular system in which the polymer-carrier combination will be used.

The blending of the comonomers with the carrier takes place prior to polymerization by absorbing the ingredients of the reaction in the solid carrier. Mechanical devices, such as a hammer or ball mill can be used in order to achieve uniform distribution. A uniform distribution of the ingredients of the reaction in the carrier can be achieved by combining the carrier and the ingredients in a solution or a slurry such as an aqueous slurry. A suitable organic solvent such as benzene or alcohol in which the monomers can be dissolved can be used. Thereafter, the dissolved monomers can be admixed with the carrier. While it is preferred to carry out the polymerization reaction in the absence of solvents or diluents, such ingredients can be used to facilitate the absorption of the monomers, or to dissipate the heat of polymerization.

The preparation of the polymeric coating is effected by subjecting the mixture to conditions fostering polymerization through ethylenically unsaturated groups. The polymerization can be induced by high energy radiation or by free radical initiators such as azo-bis-isobutyronitrile, *t*-butyl peroxyphthalate, benzoyl peroxide or the like. The reaction is preferably carried out in the absence of free oxygen, conveniently under a blanket of a neutral or inert gas.

The following examples will serve to further illustrate the practice of the invention with greater particularity although it is to be understood that the invention is not limited thereto. Unless otherwise stated, all percentages and parts referred to herein are by weight.

EXAMPLE 1

200 grams of a diatomaceous earth produced under the name "Celite 503" by the Johns-Manville Corp. are charged into a 2 litre kettle. "Celite" is a Trade Mark. The contents of the kettle are heated to 80°C., then the kettle is attached to a vacuum pump, and the pressure in the kettle is reduced to 30 millimetres of mercury. The temperature and the vacuum are held for four hours in order to remove occluded air, and then the system is cooled to 25°C.

A mixture of 380 grams of N-vinyl-2-pyrrolidone, 20 grams divinyl benzene and 1 gram azo-bis-isobutyronitrile is added to the "Celite", and then the vacuum is broken with nitrogen. Heating is started, and the mixture is heated to 60°C. At this point the heating is stopped, and cooling is started with the help of the exterior ice-water cooling bath. The temperature peaks at 112°C., then it is brought back to 90°C., and is then maintained for four hours. The system is then cooled to 25°C.

The reaction product, a grayish-white material is placed in a Soxhlet apparatus and extracted with ether to remove the unreacted monomer. Then the reaction product is slurried in water and filtered through an 80 mesh screen (U.S. standard) in a pressure filter to remove uncoated fines. The cake is reslurried in water and the slurry is centrifuged and washed until the effluent is negative for vinyl pyrrolidone. It is then extracted again for sixteen hours with ether and washed with water on the centrifuge in order to remove uncross-linked polyvinyl pyrrolidone. Finally the material is placed in a vacuum oven and dried at 65°C. The dry polymer-carrier combination is ball-milled.

The final product has a nitrogen content of 2.8%, equivalent to 22.2% vinyl pyrrolidone.

EXAMPLE 2

Into a 1 litre kettle are charged, in the following order, 400 grams distilled water, 50 grams "Celite" 503, 5 grams N-vinyl-2-pyrrolidone and 1 gram ethylidene-bis-vinyl pyrrolidone.

The system is purged by nitrogen and then contents of the kettle are heated to 80°C. At this temperature, 0.25 gram azo-bis-isobutyronitrile is introduced. The mixture is stirred for one hour at 80°C. and then cooled to room temperature.

The mixture is slurried in 500 millilitres of distilled water and stirred for one hour. After filtration, the polymer-carrier system is reslurried in 800 millilitres water and stirred for one hour. This treatment is followed by a third extraction with 300 ml water. Finally, the product is filtered and dried *in vacuo* at 65°C.

The final product has a nitrogen content of 5.89%, equivalent to 46.7% cross-linked polyvinylpyrrolidone.

EXAMPLE 3

The procedure of Example 1 is followed, except that the carrier is glass-helices, and the charge is as follows: 320 grams N-vinyl-2-pyrrolidone, 60 grams dimethyl-aminoethyl methacrylate, 20 grams divinyl benzene, 1 gram *t*-butyl-peroxy pivalate. Substantially similar results are obtained.

EXAMPLE 4

The procedure of Example 1 is followed, except that the carrier is beads of silicon rubber, and the charge is as follows: 320 grams N-vinyl-2-pyrrolidone, 60 grams 4-vinyl pyridine, 20 grams allyl methacrylate, 1 gram benzoyl peroxide. Substantially similar results are obtained.

The preferred polymer-carrier systems illustrative of the present invention have unique characteristics which are essential in their use as selective adsorbents. The polymer coating is very thinly distributed, but completely covers the large surface area of the porous carrier, thus providing an increased efficiency per gram of polymer used, as compared with systems which do not employ the preferred features of the present invention. The polymer film on the surface of the carrier has shape-stability because of the heavy cross-linking which is achieved. The cross-linking limits the extent of swelling which carriers can undergo, thus keeping the total surface of the polymer film available over the total surface of the carrier. The heavy cross-linking renders the polymer completely insoluble. This property is very important, especially when these materials are used as a selective adsorbent in food, industrial, pharmaceutical or medical applications.

Examples of the selective adsorbent applications of the polymer-carrier systems illustrative of the present invention include their use in removing harmful solutes from liquids, such as proteinaceous complexes, tannins and phenols; and their use in concentrating and recovering valuable solutes such as enzymes, noble and rare metals from solutions in which they are present in very small or trace amounts, as well as their use in the adsorption of gases and vapours.

The following example illustrates the suitability of the illustrative polymer-carrier systems of the present invention as selective adsorbents.

EXAMPLE 5

13.81 grams of salicylic acid are dissolved in 500 ml. methanol and diluted to one litre with distilled water. 64.5 grams of the resulting solution is placed in an 8 oz. bottle together with 6.76 grams of the cross-linked poly(N-vinyl-2-pyrrolidone) on "Celite" selective adsorbent prepared in the manner described in Example 1. This latter amount of selective adsorbent corresponds to 1.5 grams of 100% active polymer. The mixture is placed on a shaker and is shaken for 5 minutes. The bottle is then removed and the contents thereof are filtered through Whatman No. 4 filter paper on an 8 cm. Buchner funnel using 23 in. vacuum. Exactly 50 ml. of the filtrate are transferred to a 250 ml. Erlenmeyer flask. After addition of 6 drops of phenolphthalein indicator, the solution is titrated to a pink endpoint with 0.1 N sodium hydroxide solution.

The adsorption efficiency (calculated as the percent difference between a treated sample and a blank) is 30.5%. Adsorption efficiencies of this magnitude render these selective adsorbents of the present invention useful, for example, as active chill-proofing agents for removal of impurities, especially of the phenolic-type, from beers, wines and the like.

WHAT WE CLAIM IS:—

1. A method of forming an insoluble, cross-linked, polymeric coating having a

- degree of shape stability on an inert carrier comprising blending *in situ* at least one monomer capable of addition polymerization through an unsaturated bond, a comonomer which contains more than one polymerizable unsaturated bond and an inert carrier and copolymerizing the monomers forming an insoluble as hereinbefore defined cross-linked coating on the inert carrier, wherein the inert carrier is selected from zeolites, alkaline earth metal oxides, alkaline earth metal hydroxides, silicon rubber, silica gels, glasses, ion-exchange resins, diatomaceous earth and mixtures of two or more thereof, and the monomer or monomers capable of addition polymerization through an unsaturated bond is/are selected from substituted and unsubstituted amides of unsaturated carboxylic acids, substituted and unsubstituted esters of unsaturated carboxylic acids, vinyl ethers, N-vinyl lactams, vinyl esters, vinyl monomers containing basic nitrogen groups therein and co-polymerizable mixtures of two or more thereof.
2. A method according to Claim 1, wherein the said comonomer is divinyl benzene, methylene-bis-acrylamide, ethylidene-bis-vinyl pyrrolidone or allylacrylate.
3. A method according to Claim 1 or Claim 2, wherein the carrier is porous.
4. A method according to any preceding claim, wherein N-vinyl-2-pyrrolidone is used as at least one said monomer capable of addition polymerization through an unsaturated bond.
5. A method according to Claim 1 substantially as herein described with particular reference to any one of Examples 1 to 4.
6. A coated product which has been obtained by the method claimed in any preceding claim.
7. A selective adsorbent comprising an inert carrier having a substantially uniform, shape-stable coating thereon of an insoluble, cross-linked polymeric film obtained by the method of any one of Claims 1 to 5.
8. A selective adsorbent according to Claim 7 substantially as herein described and exemplified.

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